

PPP and CNDO Calculations for Protonated Molecules

MARGARET L. BAILEY* and J. P. M. BAILEY

Mathematical Institute, University of Oxford

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CNDO calculations have been used to obtain the one-centre core integrals for protonated azines required in calculating the $\pi \rightarrow \pi^*$ absorption spectra of such molecules using the PPP method. Calculated spectra for both the parent and the protonated molecules are obtained in satisfactory agreement with experiment. The changes in the σ -framework of the molecules on protonation are also discussed in terms of the CNDO results.

CNDO-Rechnungen wurden benutzt, um die Einzentren-Rumpf-Integrale für protonierte Azine zu erhalten, die bei der Berechnung der $\pi \rightarrow \pi^*$ -Absorptionsspektren mit Hilfe der PPP-Methode benötigt werden.

Die berechneten Spektren für die Ausgangsmoleküle und die protonierten Moleküle sind in zufriedenstellender Übereinstimmung mit dem Experiment. Die Veränderungen im σ -Rumpf der Moleküle bei der Protonierung werden ebenfalls mit Hilfe der CNDO-Resultate diskutiert.

Des CNDO ont été utilisés pour obtenir les intégrales de coeur monocentriques des azines protonées nécessaires au calcul de leur spectre d'absorption $\pi - \pi^*$ par la méthode PPP. Les spectres calculés pour les molécules protonées ou non sont en accord satisfaisant avec l'expérience. Les modifications subies lors de la protonation par le squelette σ sont discutées en fonction des résultats des calculs CNDO.

Introduction

Molecules containing aza-nitrogens can become protonated under certain experimental conditions, resulting in shifts in the positions of the absorption bands. Although the PPP π -electron method [1] successfully predicts the $\pi \rightarrow \pi^*$ absorption spectra of the parent molecules, difficulties arise in applying the method to the protonated species. Protonation leads to changes in the σ -framework, which should be taken into account in the π -electron calculations; in this work it is assumed that these changes can be accounted for in the π -electron calculations through the one-centre core integrals (the core parameters). A systematic and non-arbitrary method of obtaining these parameters is discussed. Absorption spectra are calculated using these parameters for the protonated forms of pyridine, quinoline, isoquinoline, acridine and proflavine (3,6-diaminoacridine).

Method

The required corrections to the PPP core parameters are obtained from two all-valence-electron calculations, one for the parent molecule, the other for its protonated species. The CNDO method [2] was chosen for these calculations since it is based on the same formalism as the PPP method, with a similar series

* Present addresses: Department of Chemistry, University of California, Berkeley, California, and IBM Research Laboratory, San Jose, California (to March 31, 1970).

of approximations and assumptions, thus enabling a direct comparison of the π -matrix elements. The formulae for the corrections to the core parameters are obtained as follows.

For a π -type atomic orbital ϕ_u centred at atom A, the diagonal F matrix element is

$$F_{uu} = -\frac{1}{2}(I_u + A_u) - (Q_A + \frac{1}{2}(P_{uu} - 1))\gamma_{AA} - \sum_{B \neq A} Q_B \gamma_{AB},$$

for a CNDO calculation [2], where I_u is the atomic ionization potential, A_u is the atomic electron affinity, Q_A is the net total charge at atom A, P_{uu} is the electron density in ϕ_u , and γ_{AB} is the Coulomb repulsion integral between valence orbitals on atoms A and B. For a PPP calculation [3], the diagonal F matrix element is

$$F_{uu} = U_{uu} + \frac{1}{2}P_{uu}\gamma_{uu} - \sum_{v \neq u} Q_v^\pi \gamma_{uv},$$

where U_{uu} is the core parameter, γ_{uu} is the γ parameter, γ_{uv} is the Coulomb repulsion integral between orbitals u and v , and Q_v^π is the net π charge for ϕ_v .

The required change ΔU_{uu} in the core parameter is obtained by comparing the ΔF_{uu} from the CNDO and PPP methods, where the Δ quantities refer to the difference between the parent molecule and the protonated species:

$$\begin{aligned} \Delta U_{uu} = & -(\Delta Q_A \gamma_{AA} + \frac{1}{2} \Delta P_{uu} (\gamma_{AA} + \gamma_{uu})) + Q_{H^+}^+ \gamma_{AH^+} \\ & - \sum_{B \neq A, H^+} \Delta Q_B \gamma_{AB} + \sum_{u \neq v} \Delta Q_v^\pi \gamma_{uv} \end{aligned} \quad (A)$$

where H^+ refers to the protonating hydrogen, and $Q_{H^+}^+$ is the net charge on this hydrogen. If the Coulomb repulsion integrals are assumed to be the same for the two methods, formula (A) simplifies to

$$\Delta U_{uu} = Q_{H^+}^+ \gamma_{AH^+} - \sum_{B \neq H^+} \Delta Q_B^\sigma \gamma_{AB} \quad (B)$$

where Q_B^σ is the net σ charge on atom B. Both formulae (A) and (B) are considered in calculating ΔU_{uu} .

Computer programs were written to perform the CNDO and PPP calculations. For the CNDO calculations, performed using the parameters of Pople and Segal [2], only the geometry of the parent molecule was specified, together with the coordinates of the protonating hydrogen; the geometry of the protonated species was assumed to be the same as that of the parent molecule. The geometry of pyridine was taken from a determination of its structure by microwave spectroscopy [4]; the geometries of the other molecules were estimated by using the geometry of pyridine for the nitrogen-containing ring. The N-H⁺ bond length was taken as 1.03 Å [5].

The spectra were calculated using a version of the PPP method in which the off-diagonal core matrix elements are calculated from the gradient of the corresponding overlap integrals [6]. The core parameters were obtained by subtracting the correction ΔU_{uu} from the usual core parameters; these, together with the other parameters required are given in set B and set 1 of Table 1 in [6]. All possible configurations constructed by promoting a single electron from an occupied to a virtual level were included in the configuration interaction calculations. The oscillator strengths were calculated by the geometric-mean method [7].

Results and Discussion

Table 1 presents the calculated spectra for pyridinium and acridinium cations obtained using the core parameters calculated from both formula (A) and formula (B), together with the experimental absorption spectra. Either formula leads to a satisfactory interpretation of the observed spectra. In Table 2 are presented the calculated and experimental absorption spectra for both the parent molecule and the protonated species, the latter being obtained with the simpler formula (B). Overall, the agreement between the calculated and experimental spectra is satisfactory for the positions of the bands.

Quinoline shows an interesting feature in that the first and second transitions are reversed on protonation. In quinoline itself, the first transition has dominant contributions from configurational wavefunctions $\chi_{m \rightarrow m+2}$ and $\chi_{m-1 \rightarrow m+1}$, where m is the highest occupied molecular orbital; the second transition consists predominantly of wavefunctions $\chi_{m \rightarrow m+1}$ and $\chi_{m-1 \rightarrow m+2}$. In quinolinium cation, the lowest transition is dominated by $\chi_{m \rightarrow m+1}$, whereas the second transition is mainly $\chi_{m-1 \rightarrow m+1}$. The $m+1$ molecular orbital is quite different in quinoline and quinolinium cation, although the other three molecular orbitals are similar. Another experimental study [11] has shown that the 1L_a transition at 4.59 eV is lowered to 3.66 eV on protonation, as predicted by the calculations.

The configuration interaction pattern is complex in both isoquinoline and isoquinolinium, no correlation being found between the parent molecule and its protonated species. The second transition in isoquinoline and the first transition in isoquinolinium cation both have $\chi_{m \rightarrow m+1}$ as a dominant contribution, which is the same pattern as is shown by quinoline and quinolinium cation, but the molecular orbitals differ more in the isoquinoline pair. Isoquinoline is different from the other molecules studied in the relative position of the nitrogen atom in the ring.

Table 1. *Calculated and experimental absorption spectra of pyridinium and acridinium cations*

a ^a		b ^a		expt ^b
Pyridinium cation				[5]
4.75 (0.12)	<i>x</i>	4.79 (0.12)	<i>x</i>	4.8 (~0.1)
5.72 (0.04)	<i>y</i>	5.44 (0.07)	<i>y</i>	5.5
7.09 (0.53)	<i>y</i>	7.13 (0.51)	<i>y</i>	
7.26 (0.20)	<i>x</i>	7.13 (0.23)	<i>x</i>	
Acridinium cation				[8]
3.27 (0.04)	<i>y</i>	3.09 (0.03)	<i>y</i>	3.08, 3.21
3.72 (0.48)	<i>x</i>	3.40 (0.44)	<i>x</i>	{3.50, 3.67,
3.76 (0.01)	<i>x</i>	3.75 (0.07)	<i>x</i>	{3.83
5.20 (0.03)	<i>y</i>	4.97 (0.04)	<i>y</i>	{4.86
5.26 (0.30)	<i>x</i>	5.25 (0.22)	<i>x</i>	{5.05
5.55 (0.02)	<i>y</i>	5.42 (0.03)	<i>y</i>	
6.00 (0.36)	<i>x</i>	5.87 (0.45)	<i>x</i>	>5.7

a Calculated using core parameters obtained from formula (A).

b Calculated using core parameters obtained from formula (B).

^a All energies are in eV; oscillator strengths are given in brackets. The y -axis passes through the aza-nitrogen and its para-carbon, the x -axis lies in the molecular plane perpendicular to the y -axis.

^b Experimental maxima are in eV; inflections are given in italics.

Table 2. Calculated and experimental absorption spectra of some azines and their protonated species

Neutral molecule			Protonated molecule			
calc ^a		expt ^b	calc ^a		expt ^b	
Pyridine					[9]	
4.91 (0.021)	x	4.93 (0.032)	4.79 (0.12)	x	4.8 (~0.1)	
6.25 (0.003)	y	6.28 (0.122)	5.44 (0.07)	y	5.5	
7.14 (0.50)	x	6.96 (0.66)	7.13 (0.51)	y		
7.16 (0.57)	y		7.13 (0.23)	x		
Quinoline					[9]	
4.13 (0.03)		3.96 (0.025)	3.10 (0.05)		see text	
4.41 (0.08)		4.59 (0.12)	3.93 (0.19)		3.96, 4.04	
5.66 (0.53)		5.51 (0.54)	5.16 (0.21)	}	5.25, 5.31	
5.96 (0.10)	}	6.08 (0.93)	5.44 (0.05)			
6.09 (0.32)			5.98 (0.21)			
Isoquinoline					[9]	
4.11 (0.03)		3.91 (0.02)	2.82 (0.05)		}	
4.54 (0.06)		4.66 (0.11)	3.99 (0.03)			
5.75 (0.56)	}	5.75 (1.02)	4.98 (0.44)		3.73, 3.81	
5.81 (0.01)						{4.35, 4.53,
6.00 (0.47)			5.16 (0.13)	}	4.66	
			5.63 (0.28)		5.48	
Acridine					[8]	
3.46 (0.07)	y	3.26	3.09 (0.03)	y	3.08, 3.21	
3.69 (0.07)	x	{3.39, 3.50,	3.40 (0.44)	x	{3.50, 3.67,	
4.39 (0.01)	x	{3.58, 3.67	3.75 (0.07)	x	{3.83	
5.11 (0.001)	y	3.83	4.97 (0.04)	y	{4.86	
5.12 (1.31)	x	4.98	5.25 (0.22)	x	{5.05	
5.19 (0.06)	x			5.42 (0.03)	y	
5.70 (0.01)	y		5.87 (0.45)	x	> 5.7	
Proflavine					[8]	
3.22 (0.02)	y	3.14	2.74 (0.68)	x	2.79	
3.23 (0.25)	x		3.43 (0.007)	y		
4.17 (0.13)	x	4.25	3.94 (0.07)	y		
4.39 (0.004)	y	4.40	4.01 (0.00)	x		
4.86 (1.13)	x	4.73	4.47 (0.13)	y	4.47	
5.00 (0.005)	x		4.70 (0.003)	x	4.75	
5.16 (0.15)	y		5.18 (0.04)	y		
5.45 (0.01)	y		5.50 (0.001)	x		
5.56 (0.01)	x		5.65 (0.53)	x	5.87	
			5.72 (0.25)	x		

^a All energies are in eV; oscillator strengths are given in brackets. The y-axis passes through the aza-nitrogen and its para-carbon, the x-axis lies in the molecular plane perpendicular to the y-axis.

^b Experimental maxima are in eV; inflections are given in italics.

For both acridine and proflavine, the first transition shifts to lower energy on protonation. This transition arises from the $\chi_{m \rightarrow m+1}$ configuration for acridine; in proflavine, however, the molecular orbitals change extensively on protonation, and it is difficult to find any correlation in this case.

The CNDO calculations show that the characteristic n level of the azines, that is the σ -type molecular orbital largely localised on the aza-nitrogen atom,

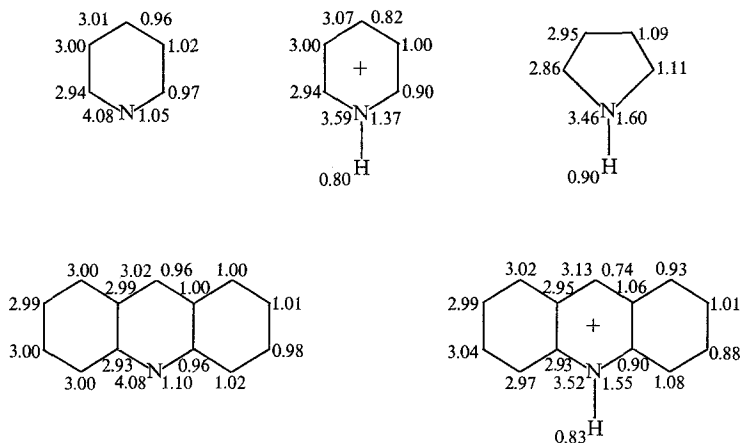


Fig. 1. σ and π electron densities from CNDO calculations

loses its n character on protonation, and is lowered in energy relative to the highest occupied π level. CNDO configuration interaction studies of pyridine and pyridinium cation indicated that the energy of the first $\sigma \rightarrow \pi^*$ transition increases markedly on protonation. In pyridine, 0.67 of the σ -electron in this $\sigma \rightarrow \pi^*$ ($n \rightarrow \pi^*$) transition comes from the nitrogen atom, whereas for pyridinium cation only 0.06 of the σ -electron comes from the nitrogen, with the remainder contributed about equally by the five carbon atoms.

The CNDO calculations indicate that the protonating hydrogen is nearly fully bonded into the aromatic system. The bond orders between this hydrogen and the adjacent nitrogen are virtually the same as in pyrrole. The net charge on this hydrogen atom, which varies from 0.20 in pyridinium cation to 0.16 in proflavinium cation, is not much greater than the corresponding value for pyrrole, namely 0.10. The σ - and π -electron densities obtained from the CNDO calculations for pyridine and acridine, and their protonated species, are presented in Fig. 1; values are also given for pyrrole for comparison. The σ - and π -electron densities of the nitrogen atoms in the protonated species are seen to be intermediate between those of pyrrolic- and aza-nitrogens. On protonation the σ -electron system has a resultant charge of +1. As would be expected, the calculations indicate a large change in the σ density at the nitrogen atom, with relatively small changes elsewhere. About 70% of the additional charge is localised within the $>N-H$ group; there is virtually no change in the σ densities at the carbon atoms adjacent to the aza-nitrogen. Although the total additional charge localised within the $>N-H$ group is about the same in all the molecules studied, there are significant variations in the two contributions Q_{H^+} and ΔQ_N^{σ} . For the remaining atoms the π densities change more on protonation than the σ densities.

The CNDO calculations enable a discussion of suitable representations of the $>N-H$ group in such systems. Neither the electrostatic model $>N: H^+$ nor the covalent model $>N^+ - H$ is in accord with the CNDO results. Since this work was completed, a paper on protonated molecules has been published [12] in which two alternative models were proposed to represent the $>N-H$ group.

Model 1 of [12] corresponds to the covalent model; in model 2 the resultant +1 charge is divided evenly between the protonating hydrogen, the protonated nitrogen and its two adjacent carbon atoms. The present work indicates that rather more of this charge should be allocated to the nitrogen atom, with the adjacent carbon atoms receiving less, so that more appropriate σ -framework core charges might be 0.25, 1.50 and 1.125 for the hydrogen, nitrogen and carbons respectively.

Conclusion

By employing both the CNDO and PPP methods, a systematic method has been found to interpret the absorption spectra of protonated azines. This approach is not limited to protonated molecules, and may be of value for other cases in which the PPP core parameters cannot be deduced easily.

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Dr. J. P. M. Bailey
Chemistry Division
P. S. F. R.
Private Bag
Petone, New Zealand